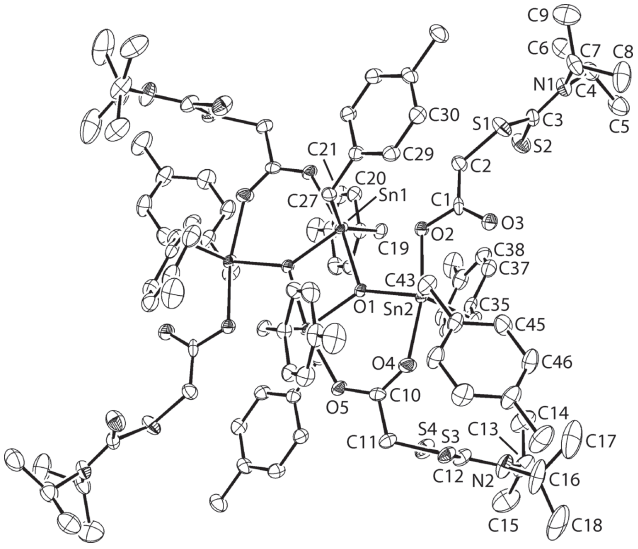
See Mun Lee, Kong Mun Lo and Edward R.T. Tiekink*

Crystal structure of bis[(μ$_3$-oxido)-(μ$_2$-(*N*,*N*-diisopropylthiocarbamoylthio)acetato-κ^2*O*,*O*′)-((*N*,*N*-diisopropylthiocarbamoylthio)acetato-κ*O*)-bis(di-4-methylbenzyl-tin(IV))], $C_{100}H_{136}N_4O_{10}S_8Sn_4$



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Abstract

$C_{100}H_{136}N_4O_{10}S_8Sn_4$, triclinic, $P\bar{1}$ (no. 2), $a = 13.7756(4)$ Å, $b = 13.9663(5)$ Å, $c = 16.6392(5)$ Å, $\alpha = 71.501(2)°$, $\beta = 73.952(2)°$, $\gamma = 63.180(2)°$, $V = 2675.49(16)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0383$, $wR_{ref}(F^2) = 0.1209$, $T = 296(2)$ K.

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The molecular structure is shown in the figure (hydrogen atoms are omitted for clarity). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The melting point (uncorrected) of the compound was measured on an electrothermal digital melting point apparatus. The elemental analysis was performed on a Perkin-Elmer EA2400 CHN analyser. The IR spectrum was recorded using a Perkin-Elmer RX1 spectrometer in a Nujol mull between KBr plates.

Di(4-methylbenzyl)tin dichloride was synthesized by the direct reaction of 4-methylbenzyl chloride (Sigma-Aldrich) and metallic tin powder (Sigma-Aldrich) in toluene according to a literature procedure [6]. The base hydrolysis of di(4-methylbenzyl)tin dichloride using 10% sodium hydroxide solution (Merck) afforded the di(4-methybenzyl)tin oxide. Diisopropyldithiocarbomylacetic acid was synthesized from diisopropylamine (Merck), carbon disulfide (Merck) and chloroacetic acid (Sigma-Aldrich) according to a literature procedure [7]. Di(4-methylbenzyl)tin oxide (0.75 g, 2.0 mmol) and diisopropyldithiocarbomylacetic acid (0.94 g, 2.0 mmol) were heated in 95% ethanol (100 mL) for 1 h until the oxide dissolved. After filtration, the filtrate was evaporated slowly until colourless crystals were formed. Yield: 0.75 g (20%). M. pt: 424–426 K. Calcd. for $C_{100}H_{136}O_{10}N_4S_8Sn_4$: C 51.19; H 6.00; N 2.45%. Found: C 50.91; H 5.88; N 2.66%. IR (cm^{-1}) 503 (*m*) ν(Sn—O), 639 (*m*) ν(Sn—O—Sn), 1411, 1378 (*s*) ν_{sym}(COO), 1662, 1597 (*s*) ν_{asym}(COO).

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.30 × 0.20 × 0.06 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.13 mm^{-1}
Diffractometer, scan mode:	CCD, φ and ω
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	25986, 13129, 0.033
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 10218
$N(param)_{refined}$:	580
Programs:	Bruker [1], SHELX [2–4], WinGX/ORTEP [5]

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.93–0.98 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$. Owing to poor agreement, five reflections, i.e. (0 0 1), (16 7 1), (1 1 1), (17 7 2) and (15 7 0), were omitted from the final cycles of refinement.

***Corresponding author: Edward R.T. Tiekink,** Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my, Edward.Tiekink@gmail.com. https://orcid.org/0000-0003-1401-1520
See Mun Lee and Kong Mun Lo: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Sn1	0.06743(2)	0.58266(2)	0.45775(2)	0.01558(7)
Sn2	0.15015(2)	0.36975(2)	0.34440(2)	0.01747(7)
S1	0.42834(8)	0.59921(9)	0.17472(7)	0.0328(2)
S2	0.26061(8)	0.78921(9)	0.07176(7)	0.0365(2)
S3	0.03115(8)	0.09307(7)	0.33558(6)	0.02718(19)
S4	−0.16901(8)	0.30322(9)	0.31429(7)	0.0360(2)
O1	0.05008(18)	0.44303(18)	0.44150(14)	0.0181(5)
O2	0.19911(18)	0.50238(19)	0.32557(15)	0.0203(5)
O3	0.3275(2)	0.4344(2)	0.22008(17)	0.0320(6)
O4	0.0680(2)	0.2578(2)	0.38506(18)	0.0297(6)
O5	−0.0586(2)	0.2745(2)	0.50262(16)	0.0236(5)
N1	0.4801(2)	0.7224(3)	0.02918(19)	0.0278(7)
N2	−0.0466(3)	0.1949(3)	0.1902(2)	0.0387(8)
C1	0.2792(3)	0.5079(3)	0.2607(2)	0.0214(7)
C2	0.2993(3)	0.6088(3)	0.2414(2)	0.0257(7)
H2A	0.297168	0.624248	0.294855	0.031*
H2B	0.240496	0.670124	0.213068	0.031*
C3	0.3925(3)	0.7092(3)	0.0837(2)	0.0244(7)
C4	0.4710(3)	0.8154(4)	−0.0479(3)	0.0363(9)
H4	0.546978	0.804128	−0.074974	0.044*
C5	0.4174(4)	0.8129(4)	−0.1156(3)	0.0470(12)
H5A	0.455285	0.742366	−0.130359	0.071*
H5B	0.421516	0.869466	−0.165831	0.071*
H5C	0.341579	0.825255	−0.093244	0.071*
C6	0.4218(4)	0.9262(4)	−0.0239(3)	0.0431(11)
H6A	0.345675	0.943736	0.000702	0.065*
H6B	0.427534	0.981909	−0.074382	0.065*
H6C	0.461102	0.922835	0.017059	0.065*
C7	0.5963(3)	0.6458(3)	0.0413(2)	0.0320(9)
H7	0.592182	0.590591	0.094576	0.038*
C8	0.6515(4)	0.5849(5)	−0.0301(3)	0.0551(14)
H8A	0.610328	0.545296	−0.031057	0.083*
H8B	0.724958	0.533998	−0.020643	0.083*
H8C	0.654391	0.636536	−0.083933	0.083*
C9	0.6587(4)	0.7049(5)	0.0541(4)	0.0548(13)
H9A	0.672227	0.753785	0.001042	0.082*
H9B	0.727629	0.651701	0.072009	0.082*
H9C	0.615653	0.746377	0.097228	0.082*
C10	−0.0019(3)	0.2298(3)	0.4408(2)	0.0199(7)
C11	−0.0161(3)	0.1306(3)	0.4375(2)	0.0267(7)
H11A	−0.093701	0.144209	0.453912	0.032*
H11B	0.022869	0.068377	0.479896	0.032*
C12	−0.0658(3)	0.2026(3)	0.2714(3)	0.0288(8)
C13	−0.1116(4)	0.2826(4)	0.1233(3)	0.0440(11)
H13	−0.079378	0.255229	0.070405	0.053*
C14	−0.0954(5)	0.3886(4)	0.1040(3)	0.0526(13)
H14A	−0.137608	0.427029	0.149119	0.079*
H14B	−0.119514	0.434147	0.050496	0.079*
H14C	−0.018788	0.371765	0.100293	0.079*
C15	−0.2307(4)	0.2978(5)	0.1402(4)	0.0631(15)
H15A	−0.235145	0.227269	0.161622	0.095*
H15B	−0.261102	0.333994	0.087830	0.095*
H15C	−0.271560	0.341978	0.181954	0.095*
C16	0.0427(5)	0.1001(4)	0.1572(3)	0.0601(16)
H16	0.077435	0.047404	0.206563	0.072*
C17	0.1312(5)	0.1337(6)	0.0943(4)	0.080(2)
H17A	0.101694	0.183376	0.043673	0.119*
H17B	0.192248	0.069402	0.079162	0.119*
H17C	0.155740	0.169417	0.120375	0.119*
C18	0.0000(6)	0.0414(5)	0.1230(4)	0.083(2)
H18A	−0.057465	0.024947	0.164866	0.124*
H18B	0.058865	−0.025889	0.111039	0.124*
H18C	−0.028785	0.087533	0.071155	0.124*
C19	−0.0052(3)	0.6997(3)	0.3498(2)	0.0219(7)
H19A	0.050772	0.723579	0.311100	0.026*
H19B	−0.022505	0.661147	0.320068	0.026*
C20	−0.1074(3)	0.8019(3)	0.3631(2)	0.0204(7)
C21	−0.0998(3)	0.8989(3)	0.3590(2)	0.0240(7)
H21	−0.030880	0.899272	0.353335	0.029*
C22	−0.1938(3)	0.9961(3)	0.3634(2)	0.0285(8)
H22	−0.186507	1.060318	0.360261	0.034*
C23	−0.2981(3)	0.9982(3)	0.3724(2)	0.0297(8)
C24	−0.3055(3)	0.9013(3)	0.3778(2)	0.0319(8)
H24	−0.374710	0.900862	0.385022	0.038*
C25	−0.2125(3)	0.8038(3)	0.3729(2)	0.0252(7)
H25	−0.220287	0.739835	0.376170	0.030*
C26	−0.3998(4)	1.1045(4)	0.3771(3)	0.0475(12)
H26A	−0.462087	1.096027	0.369836	0.071*
H26B	−0.388025	1.163411	0.332436	0.071*
H26C	−0.413611	1.121115	0.431909	0.071*
C27	0.2161(3)	0.4893(3)	0.5129(2)	0.0215(7)
H27A	0.200636	0.501921	0.570031	0.026*
H27B	0.234015	0.411858	0.519487	0.026*
C28	0.3165(3)	0.5108(3)	0.4661(2)	0.0216(7)
C29	0.4042(3)	0.4359(3)	0.4217(2)	0.0244(7)
H29	0.400849	0.370730	0.422148	0.029*
C30	0.4958(3)	0.4572(3)	0.3772(2)	0.0261(7)
H30	0.552788	0.406344	0.347780	0.031*
C31	0.5042(3)	0.5531(3)	0.3756(2)	0.0245(7)
C32	0.4193(3)	0.6256(3)	0.4220(2)	0.0262(7)
H32	0.424730	0.688937	0.423619	0.031*
C33	0.3261(3)	0.6058(3)	0.4663(2)	0.0236(7)
H33	0.269733	0.656358	0.496266	0.028*
C34	0.6023(3)	0.5793(4)	0.3252(3)	0.0338(9)
H34A	0.667105	0.512118	0.324875	0.051*
H34B	0.612363	0.625563	0.351491	0.051*
H34C	0.589740	0.616719	0.267361	0.051*
C35	0.0938(3)	0.4180(3)	0.2241(2)	0.0253(7)
H35A	0.157492	0.399247	0.179796	0.030*
H35B	0.052988	0.375255	0.227274	0.030*
C36	0.0219(3)	0.5382(3)	0.1976(2)	0.0249(7)
C37	0.0662(3)	0.6143(3)	0.1495(2)	0.0276(8)
H37	0.141704	0.590471	0.130369	0.033*
C38	−0.0006(3)	0.7255(3)	0.1297(2)	0.0318(8)
H38	0.031229	0.775083	0.097883	0.038*
C39	−0.1138(3)	0.7649(3)	0.1560(3)	0.0341(9)
C40	−0.1582(3)	0.6886(4)	0.2019(3)	0.0344(9)
H40	−0.234062	0.712510	0.219008	0.041*
C41	−0.0917(3)	0.5761(3)	0.2231(2)	0.0292(8)
H41	−0.123594	0.526435	0.254481	0.035*
C42	−0.1848(4)	0.8859(4)	0.1388(3)	0.0505(12)

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
H42A	−0.255132	0.897749	0.128725	0.076*
H42B	−0.149809	0.923386	0.089199	0.076*
H42C	−0.194958	0.914038	0.187564	0.076*
C43	0.2986(3)	0.2319(3)	0.3784(3)	0.0279(8)
H43A	0.360903	0.252456	0.354138	0.033*
H43B	0.294110	0.210778	0.440337	0.033*
C44	0.3154(3)	0.1361(3)	0.3456(2)	0.0257(7)
C45	0.3446(3)	0.1391(3)	0.2577(3)	0.0326(9)
H45	0.356714	0.199449	0.219999	0.039*
C46	0.3557(4)	0.0538(3)	0.2257(3)	0.0374(10)
H46	0.375480	0.057846	0.166963	0.045*
C47	0.3380(3)	−0.0371(3)	0.2791(3)	0.0352(9)
C48	0.3114(4)	−0.0413(3)	0.3668(3)	0.0363(9)
H48	0.300875	−0.102408	0.404493	0.044*
C49	0.3004(3)	0.0441(3)	0.3993(3)	0.0325(9)
H49	0.282499	0.039028	0.458175	0.039*
C50	0.3471(5)	−0.1277(4)	0.2428(3)	0.0539(13)
H50A	0.322138	−0.096562	0.188139	0.081*
H50B	0.302517	−0.165096	0.281434	0.081*
H50C	0.422555	−0.179160	0.235740	0.081*

Comment

Organotin(IV) carboxylates have been widely investigated because of their structural diversity [8] and their potential biological properties, in particular anti-tumour potential [9, 10]. In addition, organotin compounds containing dithiocarbamate anions have also received much attention due to their promising anti-fungal, anti-bacterial and anti-tumour activities [11, 12]. In continuation of our efforts in exploring the coordination chemistry and anti-proliferative activities of organotin carboxylates, herein the synthesis and structural features of an organotin compound with a carboxylate ligand containing a dithiocarbamate fragment are described.

The title compound is a centrosymmetric, tetra-nuclear species shown in the figure (50% displacement ellipsoids; unlabelled atoms are related by the symmetry operation (i): $-x$, $1-y$, $1-z$). The molecule is constructed about a central Sn_2O_2 core with Sn1—O1, O1^{i} bond lengths of 2.173(2) and 2.050(2) Å, respectively. Connected to this ring is the exocyclic Sn2 atom [Sn2—O1 = 2.026(2) Å]. The additional link between the endocyclic-Sn1 and exocyclic-Sn2 atoms is provided by an almost symmetrically bridging carboxylate ligand [Sn2—O4 = 2.164(2) Å and Sn1—O5 = 2.237(2) Å]. The exocyclic-Sn2 atom is also coordinated by a monodentate carboxylate ligand [Sn2—O2 = 2.151(2) Å] with the Sn2···O3 separation of 3.012(3) Å considered too long for a significant bonding interaction. There is some evidence for the O2 atom semi-bridging the Sn1 atom as the Sn1···O2 separation is 2.628(2) Å. The five-coordinate geometries for each of the Sn1 and Sn2 atoms is completed by two carbon atoms derived from the benzyl substituents. To a first approximation, the C_2O_3 donor sets define distorted trigonal bipyramidal geometries with O1—Sn1—O5 [168.41(9)°] and O2—Sn2—O4 [165.91(9)°] axial angles. Each of the carboxylate ligands is twisted as seen in the dihedral angles between the CO_2 and CS_2 residues of 70.0(4) and 81.3(3)° for the O2- and O4-carboxylate ligands, respectively.

Molecules stack in columns along the *a* axis being sustained by tolyl-Me—*C*—*H*···*S*(thione) [C34—H34*a*···S4^{ii}: H34*a*···S4^{ii} = 2.79 Å, C34···S4^{ii} = 3.741(5) Å with an angle at H34*a* = 169° for symmetry operation (ii) $1+x$, y, z] and π···π interactions between centrosymmetrically related tolyl moieties [inter-centroid *Cg*(C28—C33)···*Cg*(C28—C33)^{iii} separation = 3.709(2) Å for symmetry operation (iii): $1-x$, $1-y$, $1-z$]. The chains assemble in the three-dimensional architecture without directional interactions between them.

Tetranuclear clusters of the general formula $\{[R_2SnX]_2O\}_2$ are common hydrolysis products of diorganotin species [13]. In keeping with this observation, there are at least five structures of this type containing dithiocarbamate-functionalized carboxylates, *i.e.* $R'_2NC(=S)SCH_2CO_2^-$. The three structures with R = n-Bu and R' = Et [14], $R'_2 = (CH_2)_4$ [15] and $R'_2 = (CH_2)_5$ [16] adopt the same structural motif as the title structure. The two structures with $R = n$-Bu and R' = Me [17] and $R = n$-Oct and $R'_2 = (CH_2CH_2)_2O$ [18] adopt essentially the same motif but the carboxylate bridge involves one oxygen atom only. Both motifs have ample precedents in the crystallographic literature of the diorganotin bis(carboxylates) [8].

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